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(54) 【発明の名称】 撥水性硬化体用組成物及び撥水性硬化体

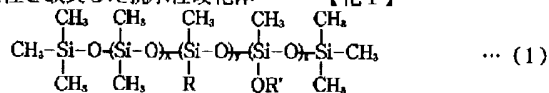
(57) 【要約】

【目的】 硬化初期の防水性及び撥水性に優れ、且つ屋外曝露条件下での耐候性も良好な撥水性硬化体が得られるのみならず、製造時の作業性を改良した撥水性硬化体

用組成物を提供することを目的とする。

【構成】 粉末状の珪酸質原料と石灰質原料とを主要成分とする硬化体用組成物に対し、下記一般式(1)

【化1】



(但し、式中Rは炭素数4～12のアルキル基、R'は炭素数1～3のアルキル基を示し、yは上記アルキル基Rの数が1分子中のケイ素原子に直結する全メチル基の

数の10モル%以上となるための整数、zは1又2であり、且つ3 ≤ x + y + z ≤ 20である。)で示されるシリコンオイルを添加する。

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] that in which this invention has weatherability in the water repellence of a hardening object -- carrying out -- water-repellent hardening suitable as an object for autoclaved lightweight concrete useful especially as a building material -- the body and its function -- it is related with a constituent and a water-repellent hardening object.

[0002]

[Description of the Prior Art] hardening which uses powder-like the nature raw material of silicic acid and a calcareous raw material as main raw materials conventionally -- the body and its function -- manufacturing a shaping hardening object is performed by a constituent's adding a frothing agent to this, or fabricating it in a predetermined configuration as additive-free, and carrying out a high pressure steam curing autoclave, low pressure steam curing, or wet curing. And the shaping hardening object acquired by doing in this way is used for the application wide range as a heat insulator, heat insulating material, concrete, mortar, a steam pipe, a slate, etc.

[0003] What ground calcareous raw materials, such as nature raw materials of silicic acid, such as silica sand and silica, lime, and cement, when autoclaved lightweight concrete was especially obtained in recent years Water is added at a suitable rate and it mixes, after adding and agitating metal powder, such as aluminum, subsequently or making air bubbles contain by the approach of mixing air, coagulation hardening is carried out, and the approach which hardens like the above by performing a high pressure steam curing autoclave, low pressure steam curing, or wet curing is adopted.

[0004] Thus, since the pore which the manufactured shaping hardening object, especially autoclaved lightweight concrete have much pores on the front face, and exists in the interior also has many open pores, absorptivity becomes high. However, it is not desirable for absorptivity to be high as a property of the autoclaved lightweight concrete used as a building material. Then, in order to prevent that the absorptivity of a shaping hardening object becomes high, adding various kinds of silicone at the time of the manufacture is proposed.

[0005] For example, in JP,55-42272,A, it is dimethylpolysiloxane, An amino-group content polysiloxane, a polyether content polysiloxane, an olefin content polysiloxane, An epoxy group content polysiloxane, a fluorine content polysiloxane, an alpha-methyl-styrene content polysiloxane, and an alcoholic denaturation polysiloxane, In a 55-85452 official report, a methylphenyl polysiloxane and a KURORU phenylmethyl polysiloxane, In a 55-90460 official report, a methyl silicone varnish, a phenylmethyl silicone varnish, and other organic monomers and polymers a blend or the thing which carried out copolymerization [these, and] Adding the denaturation silicone varnish which denaturalized with alkyd, epoxy, or acrylic resin as water repellent is indicated.

[0006] By adding the above-mentioned various silicone as water repellent, although there is a difference of extent, it is prevented that the absorptivity of the shaping hardening object which is acquired in all cases becomes high, and it comes to show water repellence and waterproofness. However, in manufacturing a shaping hardening object, in order to show strong water repellence, it did not dissolve in

the slurry which mixed the nature raw material of silicic acid a calcareous raw material, etc. and water at all, but since there was also no hydrophilic property, each various above-mentioned silicone had the problem of following difficulty on the distribution to a slurry very much.

[0007] Then, in order to solve the above-mentioned problem, the approach of emulsifying dimethylpolysiloxane, a methylphenyl polysiloxane, methyl hydrogen polysiloxane, or a methyl carboxyl denaturation polysiloxane with an anion system surfactant to JP,57-123851,A, and adding to a slurry is indicated. According to this approach, it became easy to add silicone to a slurry, but in order to use the powerful surfactant of a hydrophilic property together, the waterproofness and water repellence of a shaping hardening object had the problem that it will be spoiled by considerable extent.

[0008] Moreover, according to examination of this invention, the shaping hardening object showed good waterproofness and good water repellence in early stages of hardening by adding the various above-mentioned water repellents, but when exposed to the outdoors, it became clear that there was a problem that these properties disappear or fall comparatively easily.

[0009] Furthermore, to JP,1-44673,B, in manufacturing a shaping hardening object, the organic radicals per silicon atom are 0.4-1.8 on an average, and it is indicating adding the organopolysiloxane which at least 10% of this has a with a carbon numbers of four or more alkyl group, and has 0.01-2.0 alkoxy groups on an average per silicon atom as water repellent.

[0010] The trouble with the above-mentioned water repellent new [of alcohol separating in an alkaline slurry, since there are many contents of an alkoxy group, although the dispersibility of a slurry is also improved in a certain within the limits since it has weatherability and the alkoxy group of a hydrophilic property exists, and polluting work environment] has become clear. Furthermore, since there were few organic radicals which demonstrate water repellence most strongly on an average as 0.4-1.8, it also had the problem that the number of organic radicals had to make [many] an addition on an average as compared with the silicone oil system which is 2.0 or more.

[0011] On the other hand, the manufacture approach of the water-repellent shaping hardening object which adds the silicone oil which has the alkyl group of carbon numbers 4-12, and does not contain the alkoxy group whose total of the siloxane unit in 1 molecule is within the limits of 2-20 pieces is indicated by JP,1-58148,B that the above-mentioned problem should be solved. According to this approach, it excels also in the waterproofness and water repellence in early stages of hardening, and is the weatherability under outdoor-exposure conditions. Although (namely, water-repellent durability) could manufacture the good water-repellent shaping hardening object, when the above-mentioned silicone oil was not improved at all and did not work very carefully about the dispersibility to the slurry at the time of manufacture, it became the water-repellent shaping hardening object with which silicone oil was unevenly distributed, and had the trouble that the waterproof and water-repellent effectiveness was reduced.

[0012] water-repellent hardening which this invention was made in view of the above-mentioned situation, and it excels in the waterproofness and water repellence in early stages of hardening and a water-repellent hardening object also with the good weatherability under outdoor-exposure conditions is not only acquired, but improved the workability at the time of manufacture -- the body and its function -- it aims at offering a constituent and a water-repellent hardening object.

[0013]

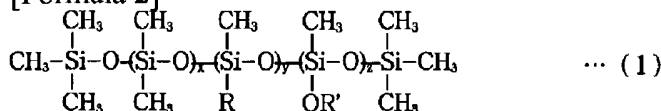
[Means for Solving the Problem and its Function] In order that this invention person may attain the above-mentioned purpose water-repellent hardening which uses powder-like the nature raw material of silicic acid and a calcareous raw material as main raw materials as a result of inquiring wholeheartedly -- the body and its function -- the workability at the time of manufacture is improved, the knowledge of the water-repellent hardening object which has the outstanding weatherability being acquired carries out, and it came to make this invention by adding to a constituent the silicone oil which has the alkyl group of the specific range, the polymerization degree of the specific range, and the alkoxy group of the hydrophilic property of the specific range that improve the dispersibility to a slurry.

[0014] namely, hardening whose this invention uses powder-like the nature raw material of silicic acid and a calcareous raw material as a major component -- the body and its function -- water-repellent

hardening preferably characterized for the silicone oil shown by the following general formula (1) by 0.05 - 3% of the weight of the thing which it comes out comparatively and is added to the above-mentioned main raw materials to a constituent -- the body and its function -- it aims at offering the water-repellent hardening object which contains the silicone oil of a constituent and a formula (1) as water repellent.

[0015]

[Formula 2]



(However, the inside R of a formula is 1 and 2, and an integer for the alkyl group of carbon numbers 4-12 and R' to show the alkyl group of carbon numbers 1-3, and for y become a number of all methyl groups of more than 10 mol % that the number of the above-mentioned alkyl group R links with the silicon atom in 1 molecule directly, and z are $3 \leq x+y+z \leq 20$.)

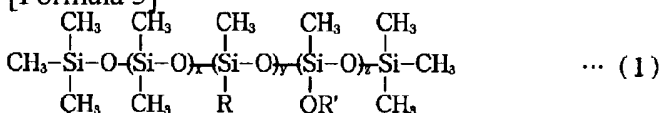
[0016] per the following and this invention -- furthermore -- if it explains in full detail -- water-repellent hardening of this invention -- the body and its function -- although the nature raw material of silicic acid and a calcareous raw material are used for a constituent as a main raw material, if these main raw materials are generally used to manufacture of a shaping hardening object, especially the class will not be restricted. Calcined lime, a limestone, slaked lime, cement, a calcium carbonate, etc. can be mentioned that what is necessary is just what can mention a silica, sand, silica, silica sand, a blast furnace slag, fly ash, etc., and includes a CaO unit as a principal component as a calcareous raw material that what is necessary is just what includes SiO₂ unit as a principal component as a nature raw material of silicic acid.

[0017] Although the blending ratio of coal of the above-mentioned nature raw material of silicic acid and a calcareous raw material is not especially limited since it changes greatly with applications of a shaping hardening object, it is usually 30:70-70:30 as a weight ratio.

[0018] The specific silicone oil used for this invention is shown by the following general formula (1).

[0019]

[Formula 3]



[0020] Although a carbon number is the long-chain alkyl group of 4-12, especially the thing of R of carbon numbers 6-10 is desirable here. When the carbon number of R is smaller than 4, weatherability is not enough, and when a carbon number is larger than 12, water repellence tends to fall. In addition, even if R in 1 molecule is the same, it may differ.

[0021] moreover, the integer which y which shows the base in the inside of 1 molecule of Above R makes more than 10 mol % of all the methyl groups that link the number of long-chain alkyl group R in silicone oil with the silicon atom in silicone oil directly -- they are more than 20 mol % and the integer more preferably made into 20-80-mol % preferably. Thereby, the weatherability of the water-repellent hardening object manufactured by this invention improves.

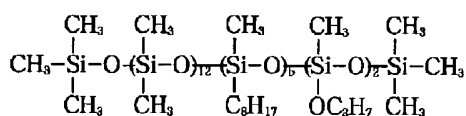
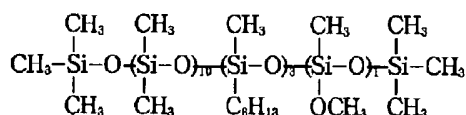
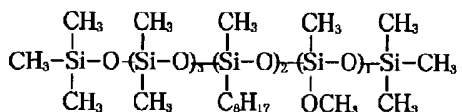
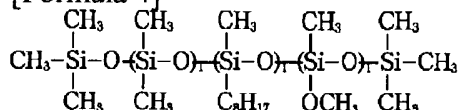
[0022] Moreover, R' is the alkyl group of carbon numbers 1-3. The carbon number of R' was set to 1-3 because [of the hydrophilic grant as an alkoxy group (OR')], and as for four or more alkoxy groups, a hydrophilic property tends to fall [a carbon number]. z which shows the base in 1 molecule of this alkoxy group is 1 or 2. It has a bad influence on the water repellence of the hardening object which will be acquired if the number of the alkoxy groups in silicone oil 1 molecule becomes three or more.

[0023] The totals (x+y+z) of the siloxane unit of the silicone oil of a formula (1) are 3-20. If the total of a siloxane unit exceeds 20, the viscosity rise of silicone oil becomes superfluous, and it will become difficult to distribute homogeneity, although an alkoxy group presents a hydrophilic property in case it mixes to a slurry.

[0024] As such silicone oil, the following compound can specifically be mentioned.

[0025]

[Formula 4]



[0026] the above-mentioned silicone oil -- the above-mentioned main raw material (the nature raw material of silicic acid, and calcareous raw material) -- receiving -- 0.05 - 3 % of the weight -- desirable -- 0.3 - 2 % of the weight -- it is added so that it may become comparatively. The hardening object which has water repellence sufficient at less than 0.05 % of the weight cannot be acquired, but if it exceeds 3 % of the weight, the water repellence beyond it will become disadvantageous economically, without being obtained.

[0027] In addition, two or more sorts can add combining the above-mentioned silicone oil, or the constituent of this invention can be added combining the above-mentioned silicone oil and the other silicone oil, although at least one sort of the above-mentioned silicone oil is added.

[0028] As the general synthetic approach of the silicone oil of the above-mentioned formula (1), the addition reaction of the long-chain alkene of carbon numbers 4-12 like $\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{CH}_3$ is carried out to the organopolysiloxane which has a specific SiH radical, and a SiH radical compounds one piece or the silicone oil which remains two or more pieces in 1 molecule, for example. Although it is very difficult to make a long-chain alkene add to the organopolysiloxane which has a SiH radical here so that it may become with 100% of conversion, it is an easy thing to make it add so that it may become about 90% of conversion. Thus, the approach of introducing an alkoxy group into the silicone oil which made the SiH radical remain for the alcohol of carbon numbers 1-3 by suitable ***** and dehydrogenation can be mentioned. According to this approach, the silicone oil of the above-mentioned formula (1) can be manufactured easily. In addition, generally as for the catalyst of the above-mentioned addition reaction and dehydrogenation, a platinum compound like chloroplatinic acid is used as a common catalyst.

[0029] The various components other than the main raw materials of the nature raw material of silicic acid mentioned above and a calcareous raw material can be added to the constituent of this invention if needed, and reinforcing materials, such as a glass fiber, a synthetic fiber, and pulp, saw dust, straight mineral oil, a hardening accelerator, etc. are mentioned to it as such a component, for example.

[0030] When acquiring a shaping hardening object using the constituent of this invention, water is added, this constituent is used as the shape of a slurry, this is slushed into a mold and a water-repellent hardening object is acquired by fabricating and recuperating oneself. Especially the constituent of this invention is more suitable as an object for autoclaved lightweight concrete by steam curing which is applied suitable for manufacture of autoclaved lightweight concrete with the consistency of 150 - 800 kg/m³, and has the consistency of 150 - 450 kg/m³ especially.

[0031]

[Effect of the Invention] water-repellent hardening of this invention -- the body and its function -- according to the constituent, the workability at the time of manufacture is improved, it excels in the waterproofness and water repellence in early stages of hardening, and a water-repellent hardening object also with the good weatherability under outdoor-exposure conditions can be manufactured easily, and a water-repellent hardening object with this hardening object suitable as autoclaved lightweight concrete of a building material since content distribution of the silicone oil of a formula (1) is carried out is acquired.

[0032] [Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0033] the detailed sand 50 section (the weight section and the following -- the same) of 70 - 80% of [example 1] silica contents, Add the water 60 section to the Portland cement 28 section, the fine powder calcined-lime 12 section of 88 - 92% of calcium-oxide contents, and the aluminium-powder 1 section, and it considers as the shape of a slurry. the organopolysiloxane A (viscosity: -- 20cst; -- 25 degrees C) shown in this slurry by the following formula (2) as silicone oil the following -- being the same -- it added at a rate shown in Table 1 to the total drained weight in a slurry, and the constituent was obtained, after slushing this constituent into the mold and carrying out steamy hardening with the autoclave of ten atmospheric pressures for 10 hours, it dried at 120 degrees C in air for 3 hours, and the hardened material was obtained.

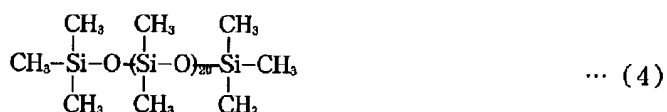
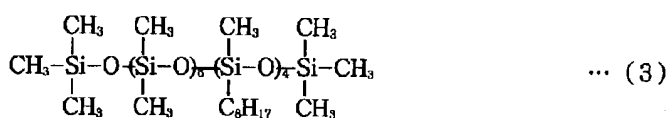
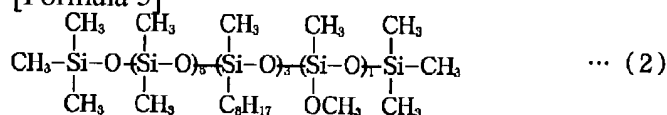
[0034] The hardened material was obtained like the example 1 except having considered as the amount which showed the addition of the organopolysiloxane A of the [examples 2 and 3] example 1 in Table 1.

[0035] The hardened material was obtained like the example 1 except having made the silicone oil of the [examples 1-3 of comparison] example 1 into the organopolysiloxane B (viscosity: 23cst) shown by the following formula (3), and having considered as the amount which showed the addition in Table 1.

[0036] The hardened material was obtained like the example 1 except having made the silicone oil of the [examples 4-6 of comparison] example 1 into the organopolysiloxane C (viscosity: 20cst) shown by the following formula (4), and having considered as the amount which showed the addition in Table 1.

[0037]

[Formula 5]



[0038] The specific gravity of each hardened material of the above-mentioned examples 1-3 and the examples 1-6 of a comparison was 0.40 - 0.45 g/cm³.

[0039] Each hardened material was cut to 10x10x3 (cm), waterdrop was dropped at three places of those front faces, and the water-repellent condition was observed. The following criteria estimated each water repellence.

[0040] O Waterdrop is kept spherical and, as for water repellence, after [of :] 30 minutes is very good.

O After [of :] 30 minutes, waterdrop becomes hemispherical, and water repellence is good.

** : Although waterdrop collapses after 10 minutes, by the time it is absorbed under a front face, it will not result, but water repellence is a little good.

x : After 5 minutes, waterdrop is absorbed under a front face, and water repellence is bad.

xx: Waterdrop is immediately absorbed under a front face and water repellence is not shown.
The water-repellent evaluation result of each hardened material is written together to Table 1.

[0041]

[Table 1]

		オルガノポリ シロキサン	添 加 量 (重量%)	硬 化 初 期 撥 水 性	100 日 曝 露 後 の 撥 水 性
実 施 例	1	A	1.0	◎	◎
	2		0.5	◎	◎
	3		0.2	◎	◎
比 較 例	1	B	1.0	◎	◎
	2		0.5	◎	◎
	3		0.2	○	○
例	4	C	1.0	◎	△
	5		0.5	○	×
	6		0.2	○	×

[0042] From the result of Table 1, even when the hardening object acquired with the constituent of this invention has few additions of silicone oil, it is admitted that good water repellence continues. On the other hand, although it has a long-chain alkyl group like the silicone oil of this invention, when the organopolysiloxane B which does not contain an alkoxy group is used (examples 1-3 of a comparison), it is admitted that water repellence falls when there are few additions of silicone oil, and water repellence does not continue. Moreover, although the water repellence in early stages of hardening is also inferior a little when the organopolysiloxane C which does not contain a long-chain alkyl group and an alkoxy group is used (examples 4-6 of a comparison), great difference is especially accepted in water-repellent durability.

[0043] The water 40 section is added to the detailed silica powder 32 section of 85% of [example 4] silica contents, the Portland cement 22 section, the powder calcined-lime 6 section, and the aluminium-powder 0.5 section, and it considers as the shape of a slurry, and is silicone oil to the slurry. After adding at a rate shown in Table 2 to the total drained weight in a slurry and agitating further the organopolysiloxane D (viscosity: 40cst) shown by the following formula (5), according to normal operation, the autoclaved lightweight concrete by steam curing was manufactured.

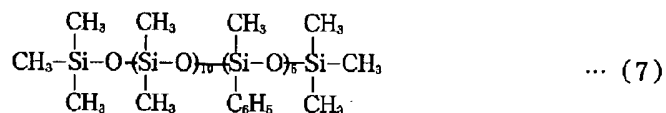
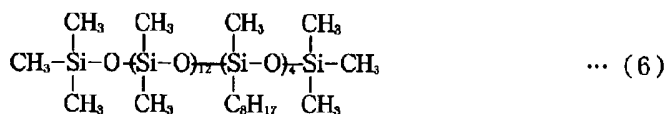
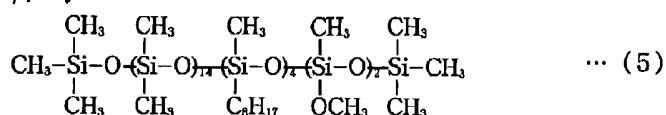
[0044] The hardened material was obtained like the example 4 except having considered as the amount which showed the addition of the organopolysiloxane D of the [examples 5 and 6] example 4 in Table 2.

[0045] The hardened material was obtained like the example 4 except having made the silicone oil of the [examples 7-9 of comparison] example 4 into the organopolysiloxane E (viscosity: 40cst) shown by the following formula (6), and having considered as the amount which showed the addition in Table 2.

[0046] The hardened material was obtained like the example 4 except having made the silicone oil of the [examples 10-12 of comparison] example 4 into the organopolysiloxane F (viscosity: 40cst) shown by the following formula (7), and having considered as the amount which showed the addition in Table 2.

[0047]

[Formula 6]



[0048] The consistency of each obtained autoclaved lightweight concrete was 280 - 300 kg/m³.

[0049] Water-repellent evaluation of each autoclaved lightweight concrete is performed like the above, and the result is written together to Table 2.

[0050]

[Table 2]

		オルガノポリ シロキサン	添 加 量 (重量%)	硬化初期 撥水性	100日曝露後 の撥水性
実 施 例	4	D	1.0	◎	◎
	5		0.5	◎	◎
	6		0.2	◎	◎
比 較 例	7	E	1.0	◎	◎
	8		0.5	◎	○
	9		0.2	○	△
例	10	F	1.0	○	×
	11		0.5	○	×
	12		0.2	×	×

[0051] From the result of Table 2, even when the autoclaved lightweight concrete manufactured by the approach of this invention has few additions of silicone oil, good water repellence is acquired, and it is admitted that water repellence continues also under exposure conditions. On the other hand, it is admitted that have a long-chain alkyl group, water repellence will fall if there are few additions of silicone oil when the organopolysiloxane E which does not contain an alkoxy group is used (examples 7-9 of a comparison), and water repellence does not continue under exposure conditions. Moreover, it has an aryl group, and although the water repellence in early stages of hardening is also inferior a little when the organopolysiloxane F which does not contain a long-chain alkyl group and an alkoxy group is used (examples 10-12 of a comparison), great difference is especially accepted in water-repellent durability.

[0052] Therefore, it was admitted from the above result that the constituent of this invention was suitable as an object for autoclaved lightweight concrete by steam curing.

[0053] One example of the silicone oil used for the constituent of [example of reference] this invention is obtained by the following synthetic approaches.

[0054] That is, SiH radical content methyopolysiloxane 423g shown by CH₃ and 3(CH₃) SiO[(CH₃) 2SiO]6[HSiO]4Si (CH₃)₃ and decene 210g were taught to the 11. 4 Thu openings flask which attached an agitator, a thermometer, Dimroth, and a dropping funnel, five drops of 1% isopropanol solutions of chloroplatinic acid were added, and it was made to react at 120 degrees C for 2 hours. Then, cooled to 60 degrees C, added methyl alcohol 30g through the dropping funnel, it was made to react at 70 degrees

C for 1 hour, and silicone oil was compounded.

[0055] As a result of infrared spectroscopy's analyzing this silicone oil, it was admitted that it was checked that SiH association and an unsaturated bond have disappeared, decene carried out the addition reaction to the SiH radical of methyopolysiloxane, and methyl alcohol carried out dehydrogenation to the residual SiH radical.

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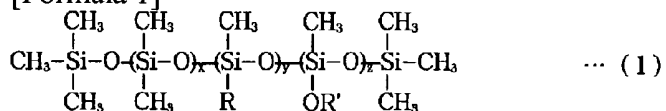
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CLAIMS

[Claim(s)]

[Claim 1] hardening which uses powder-like the nature raw material of silicic acid and a calcareous raw material as a major component -- the body and its function -- a constituent -- the following general formula (1)

[Formula 1]



(-- however, an integer for the alkyl group of carbon numbers 4-12 and R' to show the alkyl group of carbon numbers 1-3 as for the inside R of a formula, and for y become a number of all methyl groups of more than 10 mol % that the number of the above-mentioned alkyl group R links with the silicon atom in 1 molecule directly and z -- 1 -- it is 2 again and is 3 <=x+y+z<=20.) -- water-repellent hardening characterized by coming to add the silicone oil shown -- the body and its function -- constituent.

[Claim 2] The water-repellent hardening object containing the silicone oil of the above-mentioned general formula (1).

[Claim 3] The water-repellent hardening object according to claim 2 which is autoclaved lightweight concrete.

[Translation done.]